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J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 30 May 2017

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Super Snowflakes: Step-Wise Self-Assembly and Dynamic Exchange of Rhombus Star-Shaped Supramolecules

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KEYWORDS Supramolecule, Terpyridine, Self-assembly, Ion mobility-mass spectrometry

ABSTRACT: With the goal of increasing the complexity of metallo-supramolecules, two rhombus star-shaped supramolecular architectures, namely super snowflakes, were designed and assembled using multiple 2,2':6',2"-terpyridine (tpy) ligands in a step-wise manner. In the design of multi-component self-assembly, ditopic and tritopic ligands were bridged through Ru(II) with strong coordination to form metal-organic ligands for the subsequent self-assembly with a hexatopic ligand and Zn(II). The combination of Ru(II)-organic ligands with high stability and Zn(II) ions with weak coordination played a key role in the self-assembly of giant heteroleptic super snowflakes, which encompassed three types of tpy-based organic ligands and two metal ions. With such step-wise strategy, the self-sorting of individual building blocks were prevented from forming the undesired assemblies, *e.g.*, small macrocycles and coordination polymers. Furthermore, the intra- and intermolecular dynamic exchange study of two super snowflakes by NMR and mass spectrometry revealed the remarkable stability of these giant supramolecular complexes.

Introduction

Self-assembly as a powerful bottom-up approach has been extensively used by nature to create complex biological systems. Synthetic supramolecular chemistry aims to use the principles of biological self-assembly to construct artificial nanostructures using molecular building blocks with desired functions and properties.[1] Among this diverse research field, coordination-driven self-assembly,[2–4] a burgeoning section of supramolecular chemistry, is flourishing for the construction of a vast variety of structures, such as helicates,[5] grids,[6] polygons,[7–9] polyhedra,[10–12] rotaxanes,[13] catenanes,[14–17] knots,[18] and links.[19] On the basis of their precisely controlled shapes and sizes, these spectacular metallo-supramolecules have found a wide array of applications, including catalysis,[16a,20] sensing,[21] drug delivery and release,[22] gas storage,[23] smart materials,[24,25] and stabilization of reactive substances.[26] Most of these achievements, however, were centered on highly symmetric metallo-supramolecules assembled by single type of organic ligand and metal ion. The corresponding abiological assemblies still suffered from a lack of complexity and thus were unable to reach the high degrees of functionality found in natural systems.

To advance supramolecular chemistry into a new level of sophistication, efforts have been made to create more complex metallo-supramolecular architectures and ultimately to achieve new chemistry and functionality. To date, the following strategies have been used to increase structural complexity and diversity issues, including i) rational design of ligands with self-sorting ability for multicomponent self-assembly;[27] ii) synthesis of multi-armed building blocks for self-assembly of multi-layered structures;[28] iii) step-wise self-assembly of heteroleptic architectures using metal-organic ligands;[29] iv) employing both coordination and dynamic covalent chemistry for subcomponent self-assembly;[12h,30] v) introducing other types of weak interactions for orthogonal self-assembly in addition to coordination.[24a,25b,31]

2,2':6',2"-terpyridine (tpy) ligands are widely used as building blocks in supramolecular and macromolecular chemistry.[2a,32] An extremely interesting aspect of this tridentate ligand is the different binding strength of tpy and transition metal ions with order as Ru(II)> Fe(II) > Ni(II) > Zn(II) > Cd(II) in the complex of $[M(tpy)_2]^{2+}$.[33] This main characteristic allows us to harness strong and weak binding metal ions, *e.g.*, Ru(II) with Fe(II), Zn(II) or Cd(II) in a step-wise manner, in which stable

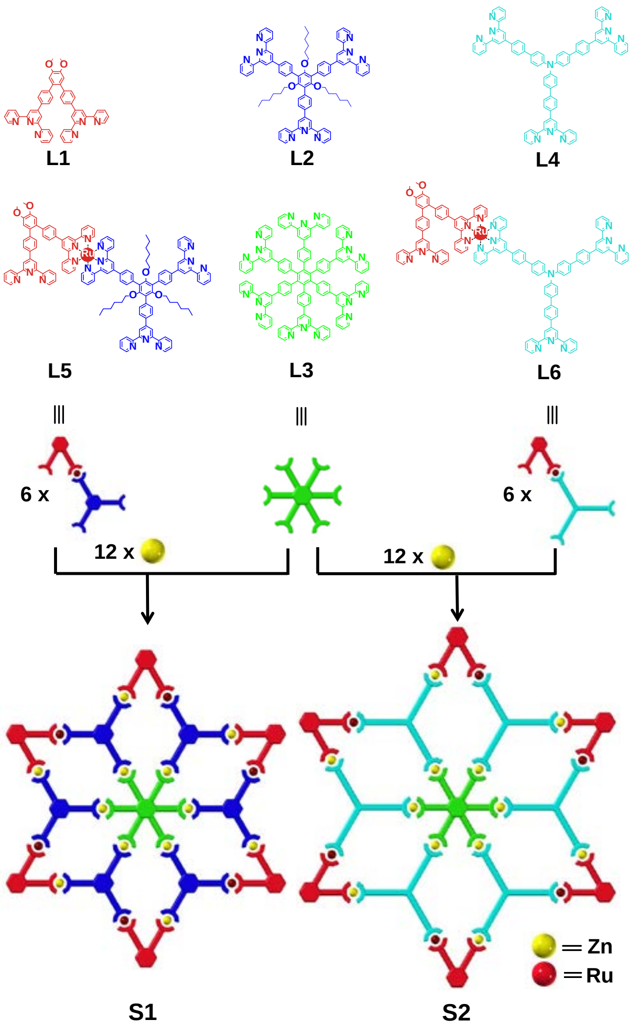
Ru(II)-organic ligand was assembled or synthesized for the subsequent self-assembly with metal ions with low binding strength and high reversibility to construct heteroleptic metallo-supramolecules with increasing complexity.[34] With this step-wise approach, most of the previous studies, however, was limited to the combination of two types of ligands and metal ions.[9a,29b−d,35] Challenges still remain by using three or more types of tpy-based organic ligands in the journey towards multi-component self-assembly.

Beyond those boundaries, we describe herein a step-wise self-assembly of giant rigid two-dimensional (2D) rhombus star-shaped supramolecules, namely super-snowflakes, which encompass three types of tpy ligands and two metal ions, *i.e.*, Ru(II) and Zn(II) in each individual structure. It is worthy to note that the pioneering snowflake-like structures by Stang[36] and Newkome[37] were based on the exo-functionalization of supramolecular hexagons using dendrimers. While our shape-persistent snowflakes were constructed with all rigid backbones. Considering that tpy-based building blocks have been introduced into infinite 2D metal–organic monolayer sheets,[38] our discrete and shape-persistent 2D supramolecular architectures may serve as a model system to investigate the self-assembly behavior and physical property in order to generate defect-free 2D materials for molecular electronics, energy storage, imaging, and sensing.

Results and Discussions

Synthesis, Self-Assembly and Characterization of Super Snowflake 1 (S1). Based on structural analysis, three tpy-based organic ligands **L1**, **L2**, and L3[39] may assemble with metal ions with ratio 6:6:1:18 to generate a snowflake-like metallo-supramolecule (Scheme S1). All three ligands were prepared through conventional Suzuki cross-coupling reactions. Direct self-assembly was conducted by successively adding methanol solution of Zn(NO$_3$) (18 eq.) into chloroform solution of **L1**/**L2**/**L3** (6:6:1) with shaking. Although the concentration of the ligands and Zn(II) solution was low (1 mg/mL), precipitate was immediately formed after the mixing. The predominant assemblies in the supernatant were identified as small triangles by ESI-MS (Figure S1, the counter ions were transformed to PF_6^-) due to the strong self-sorting ability of **L1**. We speculated that the precipitate was the 2D coordination polymers assembled by ligands **L2** and **L3** with Zn(II).[38] To block the self-sorting individual ligands, ruthenium chemistry was employed to prepare **L5** by bridging **L1** and **L2** (Scheme S3.) in the first step. Briefly, **L5** was synthesized by Suzuki coupling reaction on a precursor **7** owing to the excellent chemical stability of tpy-Ru(II) complexes during conventional coupling reaction and column separation. Note that **L5** was not able to be obtained by direct mixing **L1**, **L2** and Ru(II) because of self-sorting and separation challenges. In the second step, Ru(II)-organic ligand **L5** were assembled with a hexatopic ligand **L3** and Zn(NO$_3$)$_2$ in an exact ratio of 6:1:12 in CHCl$_3$/MeOH at 50 °C for 5 hours. The red precipitate of **S1** was obtained by adding excess amount of NH$_4$PF$_6$ into the assembly mixture, and purified by repeating wash with DI water.

Figure 1 shows the ^{1}H NMR spectra of ligand **L3**, **L5** and their corresponding complex **S1**. Sharp and well-splitting signals can be figured out in the spectra of **L3** and **L5**, which are assigned to one and four sets of tpy-phenyl units, respectively, according to the characteristic resonance peaks of tpy$H^{3',5'}$. After complexation, **S1** shows slightly broad NMR pattern in the aromatic region with six types of tpy (A-F), due to the overlap of the resonance signals ascribed to the protons in each ligand. All the 3', 5' protons on the metal free tpy units of **L3** and **L5**, *i.e.*, A(E)$^{3',5'}$, D$^{3',5'}$, and F$^{3',5'}$, were significantly shifted to downfield (~0.3 ppm) after coordinating with Zn(II) ion, owing to the electron deficiency of these protons brought about by the metal ions.[40] By contrast, all the 6,6" protons of the above mentioned tpy groups were dramatically shifted towards upfield (~0.8 ppm), due to the electron shielding effect.[40] The methoxyl groups of **L5** showed distinguished NMR peaks because of their various distance from the metal ion. While in the complex, the corresponding signal was singlet and relatively sharp, suggesting the combination of D-tpy group with Zn(II) to form a unique structure. In the alkyl region, the overlapped signals of the terminal methyl on the hexyloxyl chain of **L5** were split into two sets of triplet peaks with an integration ratio of 2:1 (Figure S42). It was indicated the formation of the designed snowflake structure, in which two of the three long alkyl chains on each arm were settled inside the snowflake structure, while the third one stayed freely outside the structure. All the assignments shown in Figure 1 are readily confirmed by the 2D-COSY, 2D-NOESY and 2D-ROESY spectra (Figures S45-46, S47-48, and S56-S57).



Scheme 1. Self-assembly of snowflakes **S1** and **S2**

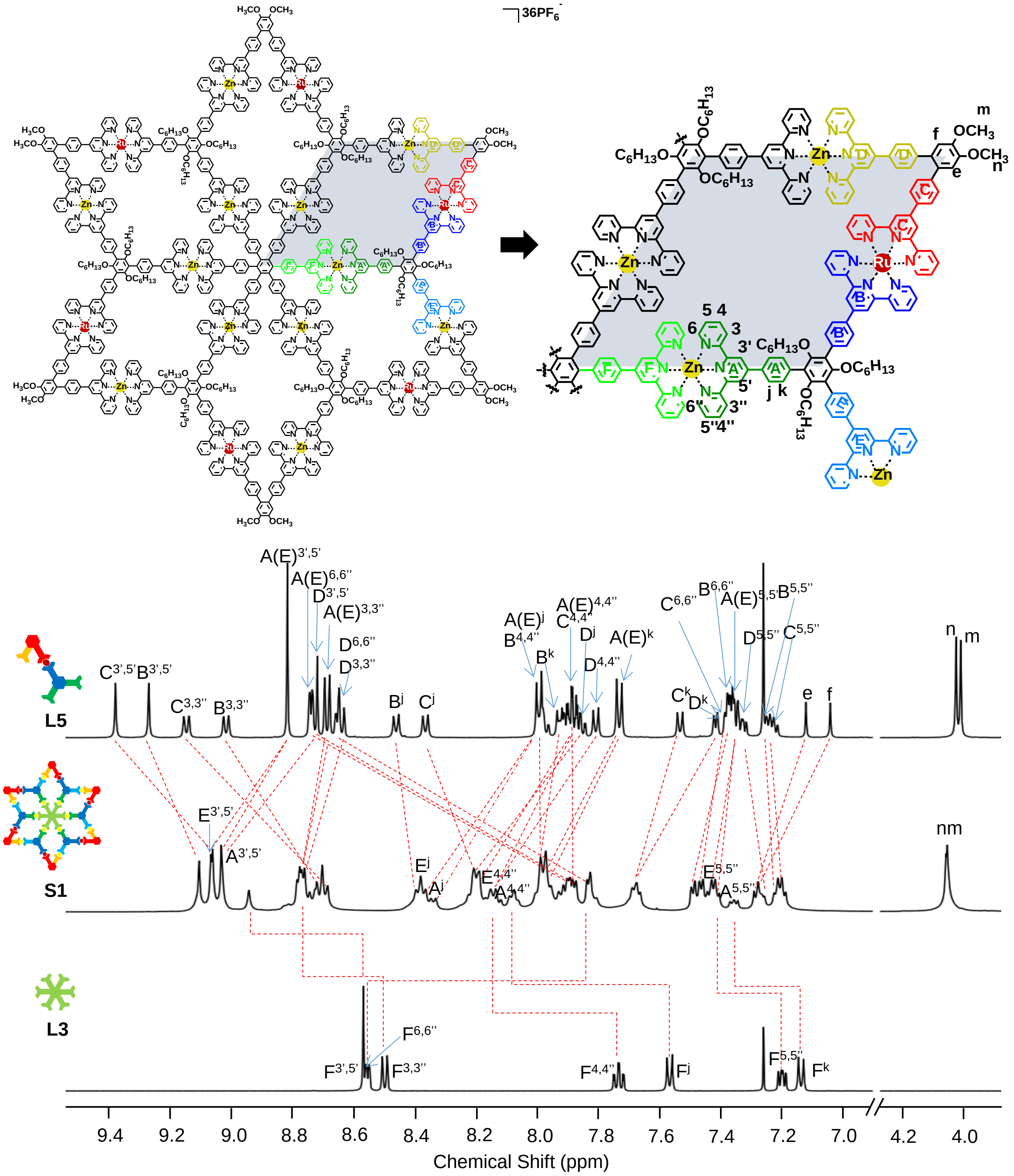


Figure 1. ^{1}H NMR spectra (500 MHz) of **L5** and **L3** in $CDCl_3$ and **S1** in CD_3CN.

The diffusion-ordered NMR spectroscopy (DOSY) provides dimensional information of **S1**, as shown in Figure 2a (full ranged spectra was shown in Figure S62). The spectrum showed a narrow band of signal with a diffusion coefficient (D) around 1.70×10^{-10} m^2s^{-1}. Using the modified Stocks-Einstein equation based on oblate spheroid model (detailed calculation procedure was summarized in SI),[41] the experimental radius, *i.e.*, the semimajor axis radius, of **S1** was 4.90 nm, which is comparable with outer radii measured from the molecular modeling of **S1** (~4.3 nm, Figure 3) with snowflake shape.

Multi-dimensional mass spectrometry, including electrospray ionization-mass spectrometry (ESI-MS), traveling wave ion mobility mass spectrometry (TWIM-MS),[42] and gradient tandem-mass spectrometry (gMS^2),[43] provide further evidences for the formation of excepted discrete assembly. One dominant set of peaks with continuous charge states from 12+ to 25+ was observed in ESI-MS (Figure 3a), due to successive loss of the counterions, PF_6^-. After deconvolution of m/z, the average measured molecular weight of the assembly is 20830 Da, which exactly agrees with the molecular composition of

S1[$(C_{137}H_{117}N_{15}O_5)_6(C_{132}H_{84}N_{18})Zn_{12}Ru_6(PF_6)_{36}$]. The experimental isotope patterns of each charge state (Figure S2) are consistent with the theoretical simulations based on the chemical composition of **S1**. We also conducted self-assembly of **L5** and **L3** with slightly different ratios of ligands and metals (Figures S67). ESI-MS showed that **S1** could be assembled even not in the perfect stoichiometry. TWIM-MS results (Figure 3b) show single set of signals with narrow distribution at each charge state (*m/z*), which unambiguously addresses that no other isomers or conformers of **S1** existed. It is suggested that the snowflake is more rigid and shape-persistent compared to the previous dendron functionalized macrocycles.[36,37]

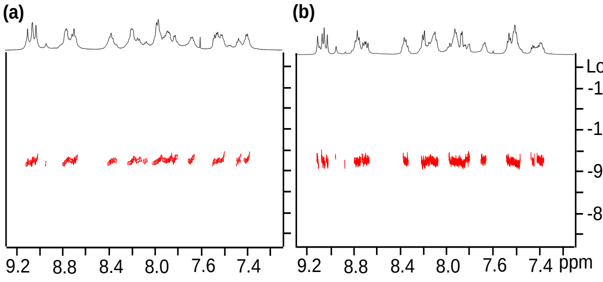


Figure 2. 2D DOSY (500 MHz, CD_3CN, 300 K) spectra of (a) **S1** and (b) **S2**.

TWIM-MS exhibits more information, *i.e.*, collision cross sections (CCSs), on the shape and size of the assemblies. CCSs data of **S1** on each charge state are summarized in Table 1, with an average value of 2959.1 Å^2. For comparison, the theoretical CCSs of **S1** were calculated based on the 70 candidate structures obtaining from each annealing cycle of energy minimized molecular model of **S1**. The averaged result of the calculated CCSs is 3054.6 Å^2 (by trajectory method),[44] which is in a good agreement with the experimental one, further convinced the snowflake shape of **S1**. gMS^2 was also employed to measure the stability of supramolecular complex. Figure 3c displays the gMS^2 results of the 17+ ions (*m/z* 1081.7) of **S1** by applying a graduate increase of collision energy from 4 V. No significant fragment peaks were observed under 16 V. All the ions were completely dissociated at 28 V, which gives a center-of-mass collision energy as 0.06 eV, and is used for the comparison with snowflake **S2**.

Transmission electron microscopy (TEM) was employed to further confirm the shape and size of the snowflake **S1** (Figure 4c). High resolution TEM imaging clearly displayed star-shaped hollow structures for **S1** with comparable size as the modeling structures. Very interestingly, these supramolecules may further self-assemble into 2D array with uniform pattern on the lacey carbon coated Cu grid. The measured diameter of these patterns from TEM (8.6 nm) was comparable with the molecular modeling diameter (8.5 nm) of **S1**. Furthermore, energy dispersive X-ray spectra (EDXS) on the TEM patterns (Figure S73) showed N, O, Ru, and Zn signals, confirming that the star-shaped pattern observed in TEM was derived from metallo-supramolecules. TEM imaging on regular carbon coated Cu grid only showed individual dots without hollow pattern, perhaps due to the background signals from the thick layer of carbon (Figure S72). We also performed TEM for other negative controls with non-ideal ratios of ligands and metals (Figures S69), but did not observe any snowflake-like pattern.

We also performed atomic-force microscopy (AFM) and scanning tunneling spectroscopy (STM) imaging for **S1**. In AFM measurement, we observed individual dots with single molecular height, which is consistent with our molecular modeling (Figure S75a-b). Note that the measured width of the molecule was much larger than the height measured by AFM and molecular modeling because of an inevitable tip broadening effect.[28f] In STM measurement (Figure S76a-b), the samples were applied to highly oriented pyrolytic graphite (HOPG) by drop-casting. Instead of observing individual supramolecules, STM showed ribbon-like nanostructures with pores. We speculated that formation of these nanoribbons were driven by the interaction between metallo-supramolecules and HOPG surface along with intermolecular interactions. This is consistent with our recent study of hierarchical self-assembly of supramolecular metal-organic nanoribbons by supramolecular concentric hexagons.[28g]

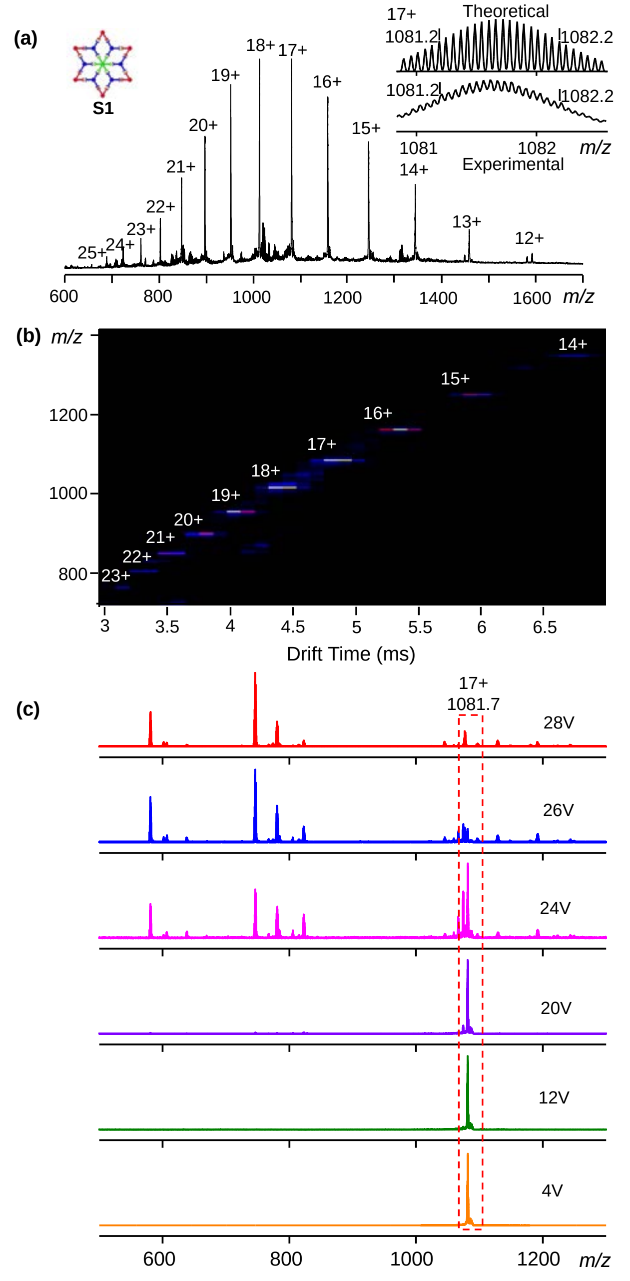


Figure 3. (a) ESI-MS and (b) TWIM-MS plot (*m/z* vs. drift time) of **S1**. (c) Gradient tandem-mass spectrometry (gMS^2) of **S1** at *m/z* 1081.7 with different collision energy.

Synthesis, Self-Assembly and Characterization of Super Snowflake 2 (S2). Encouraged by the success of **S1**, Ru(II)-organic ligand **L6** with similar geometry but slightly different length was designed for the self-assembly of snowflake **S2** with **L3**. The major difference is the phenyl group in **L5** was replaced by a triphenylamine moiety in **L6**. With such design, we might be able to assemble a larger version of super snowflake **S2** with diameter around 9.4 nm according to molecular modeling (Figure 4b), in which no significant structural distortion was observed. We expected that this robust snowflake system was readily accommodate the variation of the ligand in the outer rim but without losing the entire structural integrity benefitting from the energy favorable features of the structure.

Similar synthetic strategy as **L5** was carried out to prepare Ru(II)-organic ligand **L6** by using tri(4-bromo-phenyl)amine as starting material (Scheme S4). And the subsequent assembly of **S2** was performed by mixing **L6**, **L3**, and $Zn(NO_3)_2$ in the stoichiometric ratio (6:1:12). The formation of the desired structure was first characterized by ^1H NMR (Figure 5), and the corresponding 2D NMR results are summarized in supporting information. The aromatic region in the spectrum of **S2** is more complicated than **S1**, because of the newly induction of three sets of phenyl protons. Nevertheless, relative sharp peaks and characteristic shifts of tpyH$^{3',5'}$ (downfield), tpyH$^{6,6''}$(upfield), methoxyl protons (merged into one peak) after the assembly together suggested the formation of unique structure via expected tpy-Zn interaction.

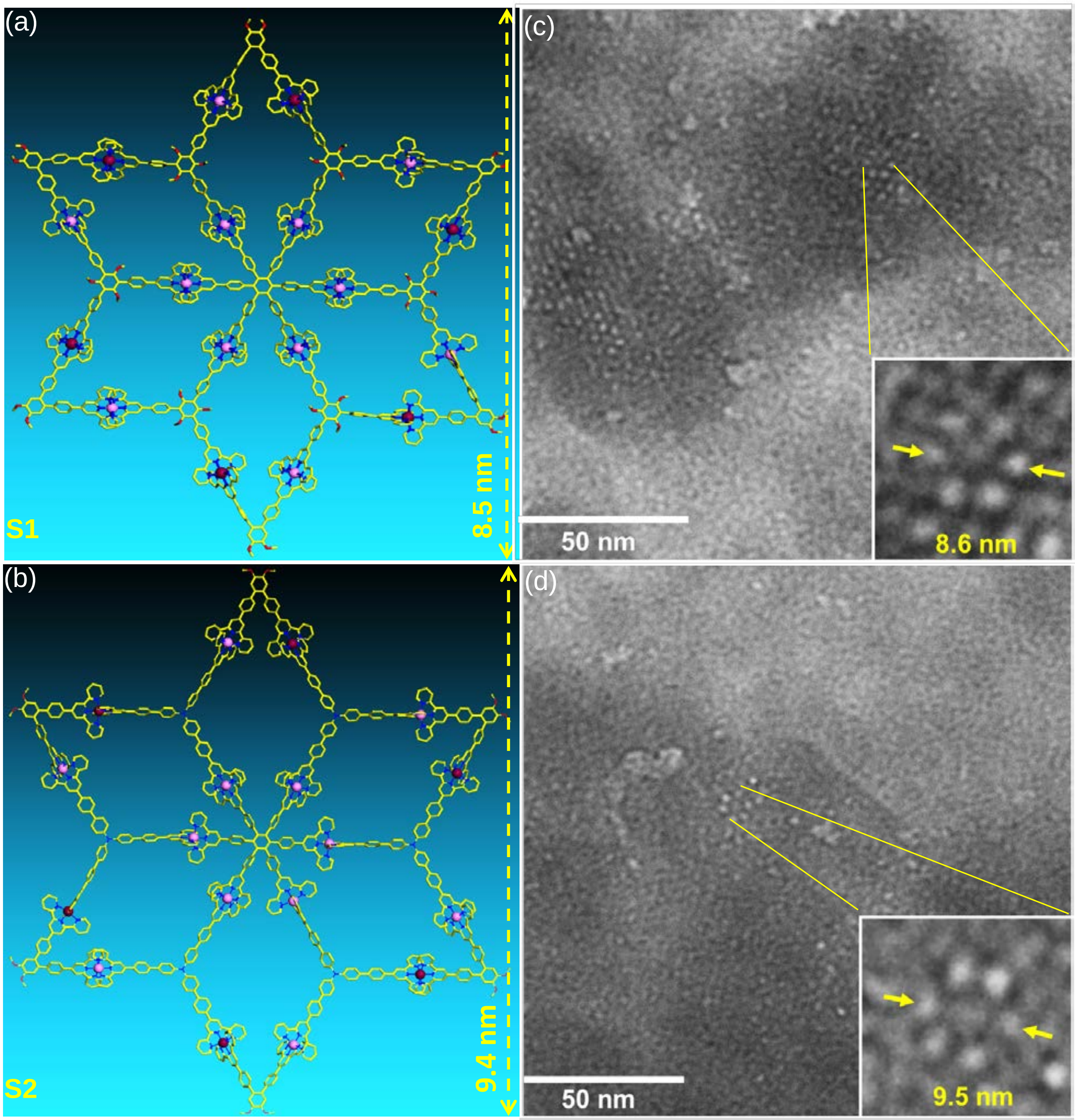


Figure 4. (a and b) Representative energy-minimized structures from molecular modelling of **S1** and **S2**. (c and d) TEM images of **S1** and **S2**.

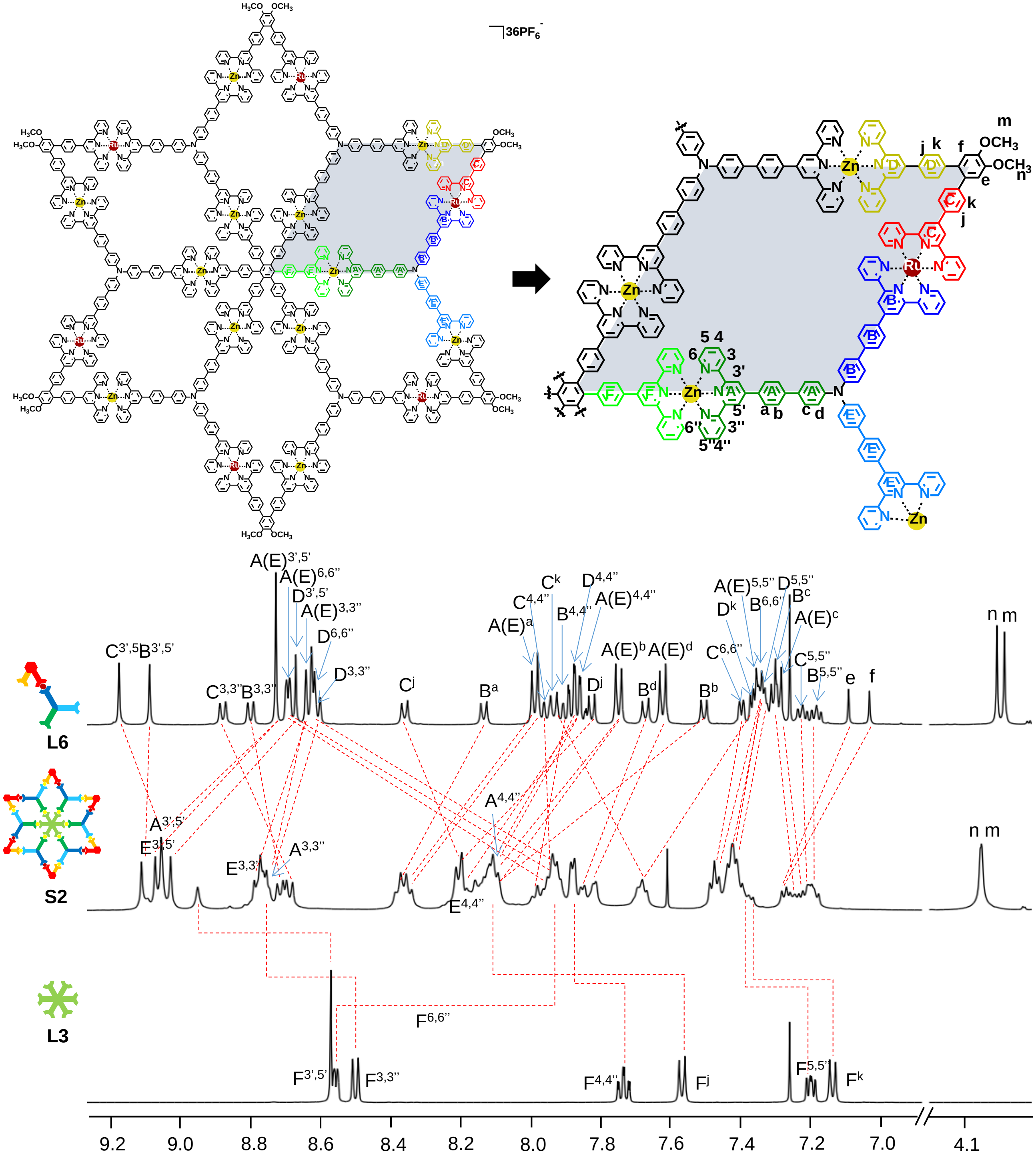


Figure 5. ^{1}H NMR spectra (500 MHz) of **L6** and **L3** in $CDCl_3$, and **S2** in CD_3CN.

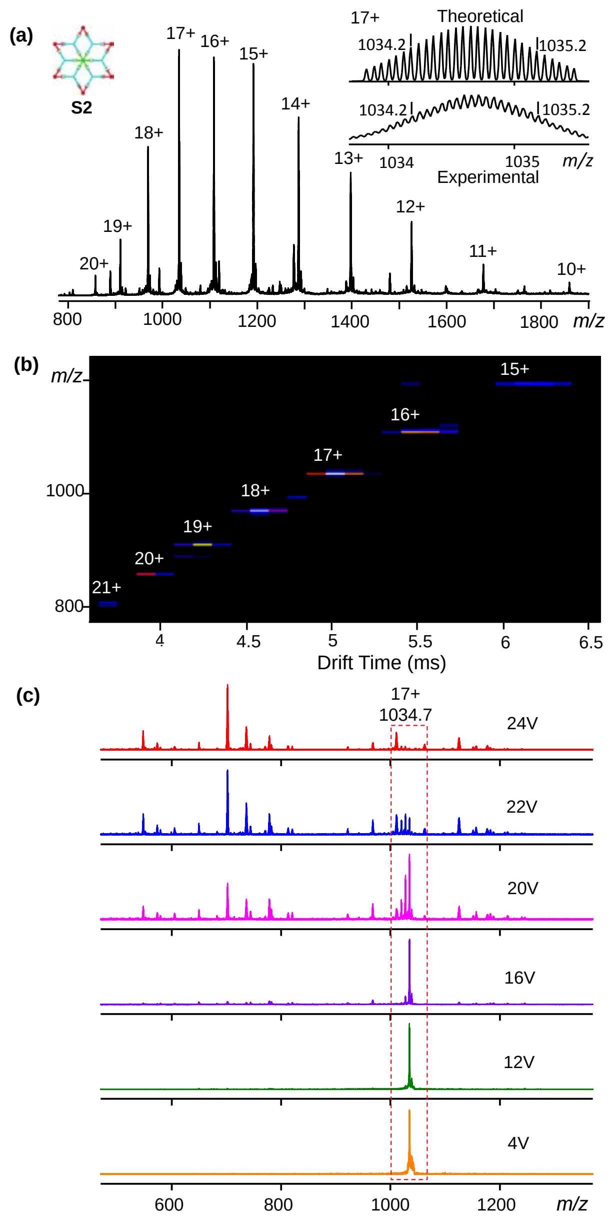


Figure 6. (a) ESI-MS and (b) TWIM-MS plot of **S2**. (c) gMS^2 of 17+ ions of **S2** at *m/z* 1034.7 with different collision energy.

ESI-MS result of **S2** (Figure 6a) displays a series of peaks with continuous charge states from 10+ to 20+. And each charge state displays well-resolved isotope patterns, which is consistent with the theoretical ones (Figure S3). The averaged measured mass of **S2** was 20030 Da, supporting its composition **[$(C_{131}H_{90}N_{16}O_2)_6(C_{132}H_{84}N_{18})Zn_{12}Ru_6(PF_6)_{36}$]**. Narrowly distributed signals of each charge state are also exhibited on TWIM-MS, indicating its exceptional rigidity and shape persistence. However, **S2** was not observed in ESI-MS for self-assembly of **L6** and **L3** with slightly different ratios of ligands and metals (Figure S68).

Experimental CCSs obtained from TWIM-MS results of **S2** were summarized in Table 1. The averaged CCS is 3059 Å^2, consistent with the averaged theoretical result (3176 Å^2). The increment of CCS value of **S2** from **S1** comes from the elongated outer rims of the snowflake as we anticipated in the design. Additionally, 2D DOSY of **S2** shows a lower value of diffusion efficiency (*D*) (Figure 2b, full ranged spectra was shown in Figure S63) with higher conducted semimajor axle radius (5.9 nm), and TEM imaging of **S2** also displays clear images of snowflake shaped patterns with narrow dispersity of diameter around 9.5 nm. (Figure 4d). TEM was also conducted for negative controls with non-ideal ratios of ligands and metals (Figure S70), but did not display any snowflake-like pattern. As **S1**, similar AFM and STM results were obtained for **S2** (Figure S75c-d, S76c-d).

Table 1. Experimental and Theoretical Collision Cross Sections (CCSs).

	Drift times [ms]	CCS [Å^2]	CCS Average [Å^2]	CCS (calcd. avg) [Å^2]
S1	6.50 (+14)	2929.5	2959.1±48.9	3054.6±64.2
	5.73 (+15)	2917.3		
	5.18 (+16)	2933.9		
	4.63 (+17)	2918.5		
	4.19 (+18)	2912.9		
	3.86 (+19)	2928.3		
	3.64 (+20)	2976.5		
	3.42 (+21)	3010.5		
	3.20 (+22)	3029.7		
	2.98 (+23)	3033.6		
S2	6.17 (+15)	3047.1	3059.0±18.2	3176.5±57.1
	5.51 (+16)	3043.4		
	4.96 (+17)	3041.8		
	4.52 (+18)	3047.7		
	4.19 (+19)	3077.3		
	3.86 (+20)	3085.2		
	3.53 (+21)	3070.7		

Further characterization of **S2** on its stability was performed by gMS^2, shown in Figure 6c. The 17+ ions (*m/z* = 1034.7) completely disappeared under 24 V, which was 4 V lower than the same situation of **S1**. This suggested the lower stability of **S2** than that of **S1**. The lower stability of **S2** was determined by its larger size, and lower density of coordination sites (DOCS)[28c,45], accordingly. DOCS provides quantitative relationship between stability and coordination site number/size (theoretical CCSs) of assemblies. With the same coordination site number, larger size brings about lower DOCS, and thus, lower stability of assembly structure. DOCS value of **S1** is 0.0118 site/Å^2, which is 5% larger than that of **S2**'s value (0.0113 site/Å^2).

Intramolecular Dynamic Exchange within S1 and S2. In both snowflakes **S1** and **S2**, there are two sets of tpy, *i.e.*, A and E from ligands **L5** and **L6**. In the scaffolds of snowflakes, a slow intramolecular dynamic exchange between A- and E-tpy may occur in **S1** and **S2** alone. Therefore, we performed detailed ROESY NMR study with a variety of mixing time to address the possible intramolecular exchange. As shown in Figures S60-S61, the cross-exchange signals of A- and E-tpy can be observed at mixing time over 200 ms, which indicated a very slow-exchange process at 300 K compared to other reported compounds with mixing time less than 100 ms.[46]

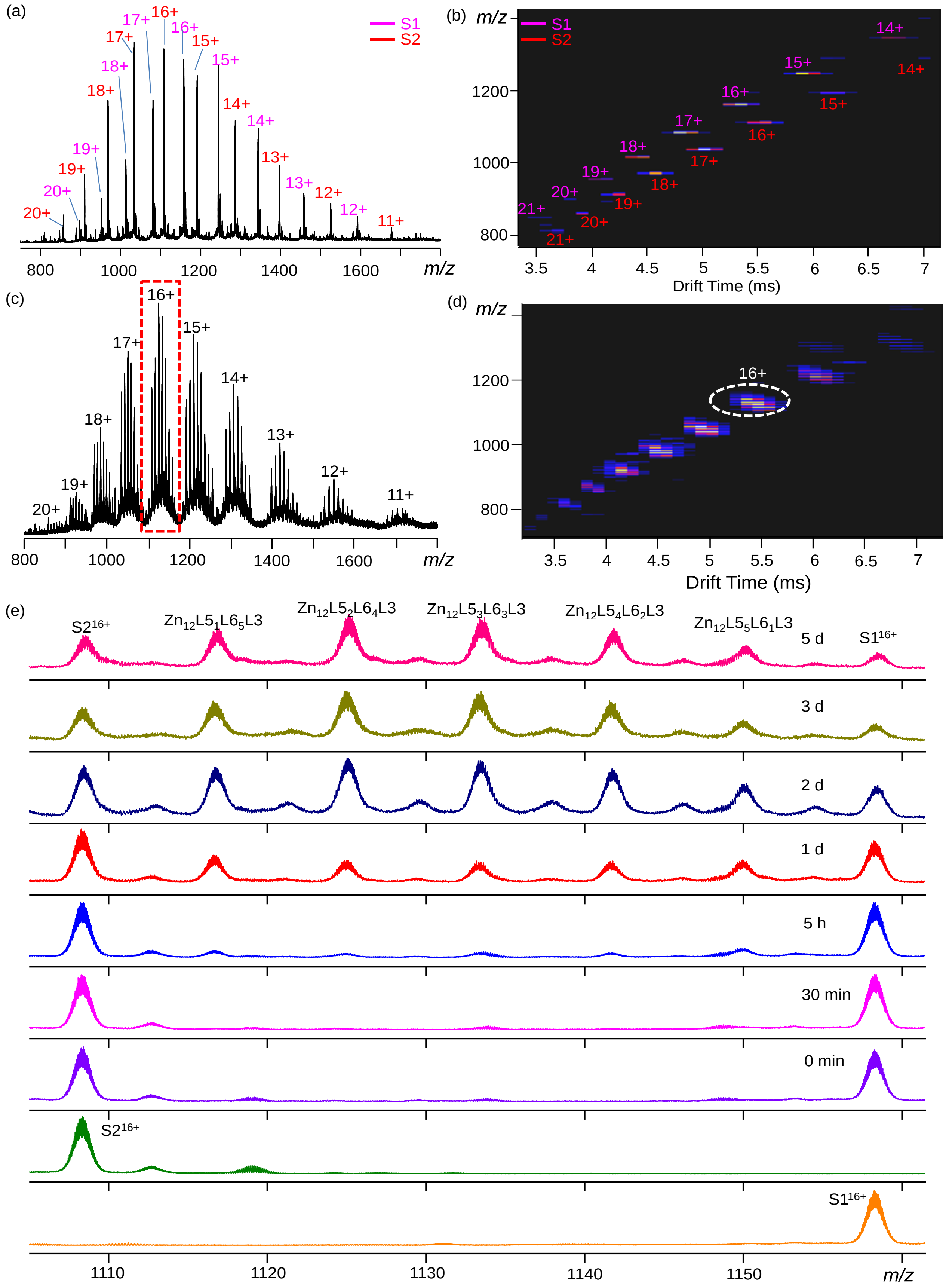


Figure 7. Dynamic exchange of preassembled **S1** and **S2**. (a) ESI-MS and (b) TWIM-MS plot of preassembled **S1** and **S2** at 0 min. (c) ESI-MS and (d) TWIM-MS plot of preassembled **S1** and **S2** at 5 d. (e) Time–dependent spectra of dynamic exchange of **S1** and **S2** at 0 min, 30 min, 5 h, 1 d, 2 d, 3 d, 5 d for expanded region of 16+ signals.

Variable temperature ^{1}H NMR was also carried out to investigate the dynamic exchange. As shown in Figure S65, the signals of 3',5'-proton of A and E-tpy group of S1 were well-splitted at 300 K with 0.034 ppm distance, which was gradually shrunk to 0.027 ppm by increasing the operating temperature to 340 K (65 ^{o}C). It indicates that the dynamic exchange of A and E-tpy can be enhanced by increasing temperature.[47] Similar emerging signals of A3',5' and E3',5' of **S2** were also recorded by variable temperature ^{1}H NMR spectra (Figure S66).

Intermolecular Dynamic Exchange between S1 and S2. In spite of the difference of ligand **L5** and **L6** in the outer rim**,** both **S1** and **S2** could be assembled with similar structures. If preassembled **S1** and **S2** were mixed in solution, the following three circumstances might occur, *i.e.*, coexistence of two discrete super snowflakes without communication, collapse and formation of unidentified complexes, or generation of hybrid snowflakes through ligand exchange. To answer the above question, preassembled **S1** and **S2** (CH_3CN, 1 mg/mL) solutions were mixed with 1:1 ratio at room temperature for dynamic behavior study. All the process was monitored by ESI-MS and TWIM-MS (Figure 7).

At 0 min after mixing, ESI-MS displayed two series of peaks corresponding to **S1** and **S2**, respectively. Remarkably, 2D separation by TWIM-MS clearly showed two sets of signals without any superimposition (Figures 7a and 7b). The slow dynamic ligand exchange started around 5 h after the mixing, indicating the great stability of each snowflake. In addition to the original peaks of **S1** and **S2**, for instance **S1**$^{16+}$ and **S2**$^{16+}$, five new peaks appeared, corresponding to all the statistical hybrid snowflakes. After 5 d, no significant change was detected by mass spectrometry. In the 2D spectrum of TWIM-MS (Figure 7d), all the hybrid signals drifted out with very similar times, suggesting they should possess the similar snowflake architectures as **S1** and **S2**. We speculated that the dynamic exchange reached equilibrium around 5 d with partial **S1** and **S2** left. To validate this assumption, a control study was performed by mixing equal molar amounts of **L5** and **L6** with **L3** and Zn(II) at 3:3:1:12 ratio. After heating at 50 ^{o}C for 15 hours, the mass spectrometry exhibited almost identical result as the one of 5 d dynamic exchange (Figure S7). Finally, we performed DOSY-NMR for the mixtures of snowflakes with high number of possible structures and isomers after complete intermolecular dynamic exchange. The measured *D* of mixture was obtained between that of **S1** and **S2** (Figure S64), indicating that those hybrid supramolecular snowflakes have the intermediate size between **S1** and **S2**.

Physical Properties. Considering the tpy and triphenylamine have been widely used in optoelectronics in both photoreceptor devices and organic light-emitting diodes,[48] we performed the following photo- and electrochemical properties study. In the absorption spectra (Figure 8a), both **S1** and **S2** show characteristic absorption bands peaked at 495 nm, corresponding to allowed metal-to-ligand charge transfer (MLCT) transitions.[49] **S2** also exhibits a unique broad absorption band located around 400 nm, which comes from intramolecular charge transfer (ICT) transition from the triphenylamine moiety to the tpy-M complex moieties.[49] The emissions of **S1** and **S2** were detected in CH_3CN solution under 73 K (Figure 8b), showing peaks at 640 nm (**S1**) and 650 nm (**S2**), respectively.

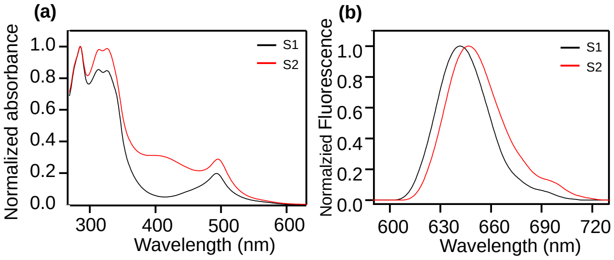


Figure 8. UV-Vis ((a), 10^{-6} M in CH_3CN, RT) and emission ((b), 10^{-6} M in CH_3CN, 73 K) of complexes of **S1** and **S2**.

The electrochemical properties of these two complexes in DMF were studied, and the results are shown in Figure 9. Both **S1** and **S2** exhibit three tpy-ligand-centered redox couples between -2.0 V to -0.5 V. Between 1.0 V to 1.5 V, **S2** showed two irreversible oxidization peaks, corresponding to the oxidization of triphenylamine moiety and Ru(II) atoms; while **S1** displayed only one oxidization peak of Ru(II). In addition, under the effect of triphenylamine group, although the peak-to-peak potential difference for each redox couple was still very similar between two complexes, potentials of each single peak of **S2** were moved to more positive value than those of **S1**.

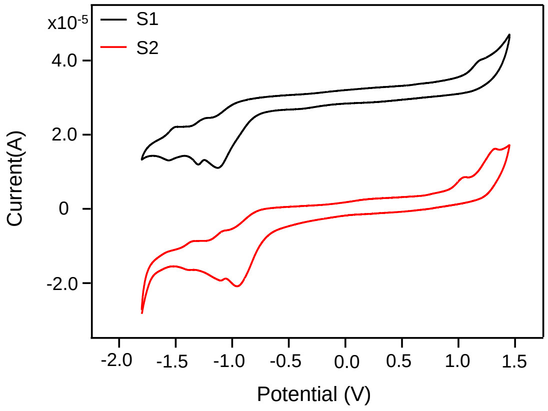


Figure 9. Cyclic voltammograms (CV) of solutions of **S1** and **S2** (performed in 0.1 M n-Bu_4NBF_4 in DMF at 298 K).

Conclusions

By utilizing the diverse coordination ability of tpy with transition metal, we have designed and assembled two snowflake supramolecules using the combination of Ru(II) and Zn(II). Instead of using direct self-assembly, such giant metallo-supramolecules were approached through step-wise synthesis strategy, which successfully prevented the formation of undesired assemblies by the self-sorting of individual ligand. For the first time, in tpy-based supramolecular field, we were able to construct complex supramolecular architectures with three types of organic ligand. Additionally, dynamic ligand exchange of two preassembled indicated that this versatile system was capable to accommodate the variation of the outer rims to form a series of hybrid snowflakes but without the entire structural integrity. We anticipate that these discrete and shape-persistent supramolecular architectures may serve as a model system for further study of the self-assembly behavior and physical property of 2D materials.

ASSOCIATED CONTENT

Supporting Information. Synthetic details, molecular modeling, ligand and complex characterization, including ^{1}H NMR, ^{13}C NMR, 2D COSY, 2D NOESY, 2D ROESY, ESI-MS, TWIM-MS and MALDI-TOF are included in supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

The authors gratefully acknowledge the support from NSF (CHE-1506722 and DMR-1205670 for X.L.; ECCS-1609788 for B.X.), Research Corporation for Science Advancement (23224 for X.L.), and ACS Petroleum Research Fund (55013-UNI3 for X.L.). Z.Z. thanks China Scholarship Council for graduate assistantship. The support of Program of Introducing Talents of Discipline to Universities of China (111 Program, B17019) is also appreciated.

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